

Geology 340 Term Paper

How are Methane Hydrates Formed, Preserved, and Released?

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Figure 1 (U.S.S.P., 2005)

Methane hydrates are an unusual sedimentary mineral that occurs in the continental shelf areas, permafrost regions, and marine sediments of the world. A hydrate is any chemical or mineral that contains water, bound within its chemical structure. Thus a methane hydrate is an assemblage of molecular methane (CH_4) molecules that are bound within a crystal lattice formed by water (H_2O) molecules. Technically, methane hydrates should be called “methane clathrates” because no hydrogen bonding occurs between the methane and water molecules as occurs in classical hydrates; however, the term “methane hydrate” has been accepted in common scientific language in addition to the more formal clathrate terminology (Rayner-Canham, 2006). Now, “clathrate” is mostly used when discussing the molecular structure of these minerals, whereas the term “hydrate” is best used when discussing accumulations of these minerals in a sedimentary bed. The general formula for a methane hydrate is $\text{CH}_4 \cdot n\text{H}_2\text{O}$ where “n” describes a variable number of water molecules within the lattice structure. This arrangement of water molecules with other gaseous molecules to form

a solid material is called a “clathrate cage” or just “clathrate.” These gas clathrates are partially held together by pressure, so they cannot exist in marine sediments above about 250 meters deep. These mysterious minerals have recently been discovered, and the techniques used to find them are still being developed. However, these methane deposits represent a tremendous energy potential if they were to be extracted and utilized. We understand that methane hydrates are formed when methane and other gases that come from decaying organic material become trapped in a clathrate crystal lattice within a defined zone of stability near the ocean floor, but there is still much more research that needs to be done in order to understand how they can be preserved, released, collected, and utilized.

Formation

The methane which eventually ends up trapped as hydrate compounds comes from microorganisms that produce methane as a byproduct of consuming buried detrital organic materials. The amount and rate of hydrate accumulation is determined by the methane supply. There are two sources of methane that contribute to hydrate formation in a defined zone of clathrate stability known as the Hydrate Stability Zone (HSZ). The HSZ exists from around 530 meters depth for northern latitudes, and around 250 meters for southern latitudes (Garg et al., 2008). The two methane sources include in situ methane generation within the HSZ and deep methane influx. For deep methane influx, natural gases like methane are produced by bacteria that decompose carbon-rich organic sediments that are buried deep within marine sediment layers, and this process provides a relatively constant influx of deep methane gas that is 99.99% pure CH_4 . Pfeffer notes that the bacteria which produce methane do so better under stressed conditions at very low retention times, but otherwise, “for intermediate retention times, hydrolysis of certain constituents of the fiber is rate limiting. At longer retention times, breakdown of the more complex fibers appear to be the rate limiting step” (Pfeffer, 1978). Pfeffer experimentally demonstrated that the nature of the organic material

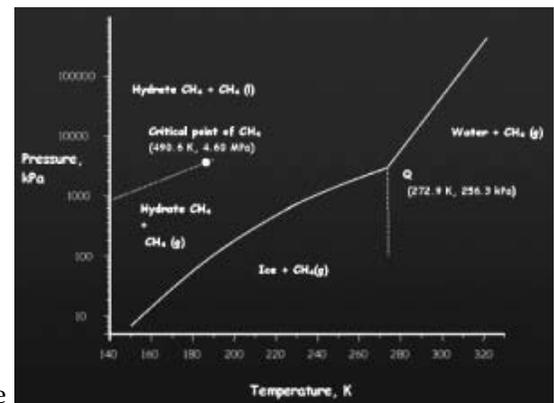


Figure 2 (Yakushev, 2003)

being decomposed, as well as the time it takes to decompose it completely, greatly affects the types and amount of natural gases produced by organic decay. Trace impurities present in the clathrates include the gases Ethane (C₂H₆), Propane (C₃H₈), Carbon Dioxide (CO₂), Nitrogen (N₂), and Hydrogen Sulfate (H₂S) (Garg et al., 2008). These trace gases-- including larger amounts of CH₄-- are also produced by in situ conversion of biomass to methane within the HSZ; however, the gases produced by in situ generation are less abundant, not as pure, and are not held as efficiently by sediments. In some areas, the influx rate of natural gases into the marine sediments has been estimated as high as 2.05 Kg·m⁻²·year⁻¹ or 128 mol·m⁻²·year⁻¹ at a given temperature of 12.3°C. Likewise, if a gas density of 78Kg·m⁻² is assumed for the sediment base boundary, the upward inflow rate would be around 26mm/year (Garg et al., 2008). Therefore, the deep methane influx process is thought to produce the majority of methane that goes into building hydrate deposits.

Clathrate formation is favored in coarse sediments as opposed to fine grained sediments. Consequently, sediment lithology plays a major role in determining where hydrate beds form (Garg et al., 2008). This is due to the coarser grained sediments having much higher permeability values than fine grained pelagic clays. When upwelling methane gas enters the HSZ, it dissolves into the pore spaces between and within sediment grains where it exists in three phases. Methane within the HSZ can exist as a free gas, dissolved in solution, or as a solid hydrate. This is because the triple point for these three phases exists at the HSZ by definition. Garg notes that if the upwelling fluid is saturated with methane, then the gas saturation level below the HSZ must be below 2-3% which is in line with the values we see from seismic data. Methane will not accumulate below this zone, nor will it be retained above the HSZ, yet at the precisely defined pressure and temperature conditions that exist at the HSZ, methane can be converted into the clathrate structure. Within the HSZ, methane clathrates are most stable on the ocean floor; however, clathrate crystals are very seldom found here due to the consumption of methane by oxidation reactions with sulfate ions present in seawater. Sulfates react with methane by the reaction:



whereby any methane present within reach of flowing seawater will be oxidized to the hydrosulfide anion and be removed from the system. Below this level, methane hydrates may take on several forms including deposits in fine grained sediments, a vein or fracture-fill deposits, or as a cementing material in high permeability sediments such as sand or volcanic ash layers (Ruppel, 2007). The solubility of methane gas in water actually increases with increasing temperature and depth, so the ascending fluids cool off as they rise and encounter regions of decreasing methane solubility, and this is when the methane crystallizes out of solution with water as it becomes more insoluble (Ruppel, 2007).

Presently, three crystal structures of methane clathrates are known to exist. The different structures are determined by the variable “n” in the generalized hydrate formula CH₄·nH₂O. In this formula, “n” refers to the stoichiometric amount of water molecules involved in building the crystal. More precisely, “n” is also the ratio of water molecules to gas molecules, and the value for “n” can vary from 5.75 to 17 (Rayner-Canham, 2006). Structure I clathrates are the most common. They have cubic symmetry and contain 46 water molecules with 8 potential gas sites. There are two smaller hexagonal dodecahedral gas sites with radii of 3.95Å, and six larger pentagonal and hexagonal spaces with radii of 4.33Å. Structure II clathrates contain 136 water molecules with 24 potential gas sites. Finally, Structure H clathrates have 34 water molecules and 6 gas sites (Ruppel, 2007).

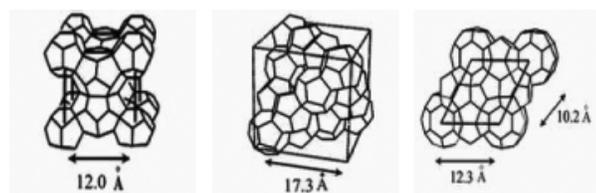


Figure 3 (Yakushev, 2003)

Once the methane is saturated in the ocean water existing between the coarse sediment grains, and the temperature and pressure are right, ice crystals will start to grow into a crystal structure that traps the dissolved CH₄ molecules inside the lattice. There is actually no chemical bond involved between the water molecules and the gas molecules other than Van der Waals forces, yet an important point is that the presence of “guest” molecules inside the

ice crystals makes the structure of the entire lattice more stable (Rayner-Canham, 2006). In fact, the presence of guest gas molecules stabilizes the structure enough to have the effect of raising the melting point of the ice to several degrees above 0°C. This is how gas clathrates, once formed, are able to persist and build up a larger depositional hydrate layer, for the clathrate structure is more stable than ice crystals or dissolved methane alone. Curiously, the identity of the gas trapped within the clathrate has little effect on the clathrate’s properties. Among the first clathrates to be synthesized in the laboratory were clathrates of the Noble Gases because this was the only type of chemistry at the time that could be done with these un-reactive gases. All gases bound in clathrates can have the same effects of stabilizing the crystal lattice provided that they are small enough to fit within the voids of

the ice crystal structure (Rayner-Canham, 2006).

Detection

Fortunately, there are many characteristics of hydrate beds that aid in their detection. Core logs provide a lot of data about gas hydrate location. Cores of marine sediment are taken and the pore water is analyzed for salinity, composition, electrical resistivity, and radioisotope abundances. One of the main isotopes used in methane hydrate detection is ^{129}I . Iodine has one stable isotope (^{127}I) and one radioisotope that is long lived ($T_{1/2}^{129}\text{I} = 15.7\text{my}$). Tomaru claims that the reason Iodine is a good tracer of gas hydrates is because there is a strong correlation with Iodine that is released by the degradation of organic matter and hydrocarbons that are produced by the same process. The evolution of methane and Iodine in situ in deep anoxic sediments will enrich sediment pore water in I relative to seawater, and this makes I a good tracer of organic material flux (Tomaru et al., 2007). Tomaru also found that pore water iodine concentrations were enriched with iodine to greater than $200\mu\text{M}$ compared with the normal seawater iodine content of $0.4\mu\text{M}$. Using variations in the $^{129}\text{I}/^{127}\text{I}$ ratio, they were able to date the pore water. The main discovery was that the iodine age was usually older than the host sediment itself, and this fact implies that the iodine and methane were created somewhere else and then migrated into the marine sediments in which they were found (Tomaru et al., 2007).

Darcy's Law: $q = -K \cdot \left(\frac{dh}{dl} \right)$ is also used to detect methane hydrate formation because the formation rate is determined by the pore fluid migration rate within marine sediments (Hornberger, 1998). The coarse sediments that favor methane hydrate formation do so because the coarse sediments have higher porosity values. This affects the value of K which is the hydraulic conductivity constant. The flow paths that the methane and iodine take from their sources to a depositional hydrate bed can then be determined by extensive core studies and carefully application of Darcy's Law. Hydrate beds may be located by finding those marine sediment beds which have high q (discharge) values that correspond with high sediment conductivity and permeability as determined by Darcy's Law. However, it does not hold true for the dissociation of hydrates near well bores because that process occurs too rapidly when hydrates are artificially dissociated.

Gas hydrate layers also act as negative impedance seismic layers. Ruppel claims that "in places, a negative impedance seismic reflector -the bottom-simulating reflector or BSR- marks the phase boundary between higher-velocity, gas hydrate-bearing sediments above and lower-velocity sediments charged with free gas below." Therefore, the seismic behavior of hydrate bed layers can also serve as a mechanism by which we can detect large gas clathrate deposits.

Additionally, methane hydrate beds may be located by the anomalous heat signature they produce. The formation of the clathrate crystal lattice is an exothermic process, and the heat that is evolved is mainly transported by convection and advection, yet this heat also goes into warming the marine sediments in the vicinity. The heat evolved by hydrate formation is given by the equation: $\Delta H = T_k \cdot \Delta V \cdot \left(\frac{dP}{dT} \right)$

In this equation, the change in enthalpy (ΔH) equals the temperature in Kelvin (T_k), multiplied by the change in volume (ΔV), and multiplied by the slope of the phase line (Garg, 2008). One implication of the equation is that as T_k increases from 273K to 313K, we see the value for ΔH increase three to four times. However, in most generalized conditions, a value for ΔH is usually given as 53.8 KJ/mol or 450KJ/Kg of hydrate formed. We take the value for ΔH to be -450KJ/Kg because for this exothermic reaction heat is evolved and leaves the system. Using this value, if 10% of the sediment pore water brine (which is 5% of the total sediment volume) is converted to the clathrate structure with a density of $920\text{Kg}/\text{m}^3$, the heat evolved per cubic meter of sediment would be equal to:

$$\Delta H = (0.05) \cdot \left(920 \frac{\text{kg}}{\text{m}^3} \right) \cdot \left(450 \frac{\text{kJ}}{\text{kg}} \right) \cdot \left(10^3 \frac{\text{J}}{\text{m}^3} \right) = 21 \frac{\text{MJ}}{\text{m}^3} \quad (\text{Garg, 2008}).$$

The latent heat energy produced by clathrate crystallization markedly warms up the marine sediments in which this process is occurring. Therefore, gas hydrate beds are often detected thermally by the latent heat of crystallization they give off to the surrounding sediments as they are forming.

Energy Potential

Before the gas hydrate discoveries in the last decade, gas hydrates were studied primarily for safety reasons in the oil industry. Methane hydrate beds often occur in the same regions as oil and natural gas reservoirs, and it was common for gas hydrates to clog wells and pipelines creating an explosion hazard to the people and property involved in oil extraction. Marine gas hydrates have the potential to damage equipment by

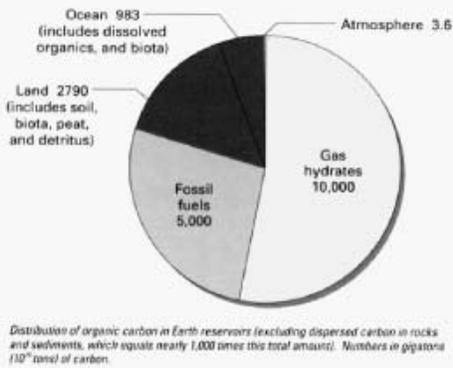


Figure 4 (Dillon, 1992)

clogging machinery or unexpectedly dissociating (Ruppel, 2007). Gas hydrates can also occur in tanks and pipes containing refined natural gas if there is any water present; therefore, it is a necessary practice to thoroughly dry any quantity of natural gas prior to the storage or transportation of it.

Today, methane hydrates represent an exciting and untapped resource that would help meet our expanding energy needs well into the future. Methane hydrate fields are almost always more accessible than oil and natural gas reservoirs located deep underground. In addition to marine settings, they have even been found in lakes and inland seas such as Lake Baikal and The Black Sea (Ruppel, 2007). In fact, a large amount of methane clathrates are also found under shallow permafrost deposits in arctic regions. A major advantage of these locations is that

the infrastructure for natural gas processing is in place from the oil industries already working up there extracting oil and natural gas, this definitely decreases the initial investment that would be required to start harvesting clathrate gas reserves. It also helps that the gases locked up in clathrate structures are naturally cracked by their ascension process, so they would require no further refinement process beyond collection and storage (Ruppel, 2007). In 2005, the United States Congress passed the Methane Hydrate Research and Development Act which set out to examine hydrate beds in the Gulf of Mexico and the Alaskan North Slope. It is clear that governments and industries are already taking a major interest in the development of methane hydrates as an energy resource in the future.

There are several important reasons why utilizing methane hydrates as an energy resource is a smart idea. First, the formation process of methane clathrates concentrates methane gas to about 160 times their gas volume at standard temperature and pressure values, so clathrates represent a highly concentrated energy source. In fact, methane is so concentrated in the clathrate structure that, if set alight, the clathrate crystals will burn in the atmosphere (see picture on first page). More importantly, the sheer amount of methane in these hydrate bed reserves is immense. Mielke states that "estimates of the amounts are speculative and range over three orders of magnitude from about 100,000 trillion cubic feet to 279,000,000 trillion cubic feet of gas. Despite the enormous range of these estimates, gas hydrates seem to be a much greater resource of natural gas than conventional accumulations" (Mielke 2000). Dr. William Dillon of the U.S. Geological survey further explains, "the worldwide amounts of carbon bound in gas hydrates is conservatively estimated to total twice the amount of carbon to be found in all known fossil fuels on Earth. The immense volumes of gas and the richness of the deposits may make methane hydrates a strong candidate for development as an energy resource" (Dillon, 1992). It would seem that because such large reserves exist, it would be prudent to investigate methods of harvesting them.

Yet another fact that makes methane a good fuel source is that it has about 80% the heat content of crude oil which is much better than most other alternative energy sources. A barrel of methane contains 4.62 million BTUs of heat energy compared to a barrel of crude oil that produces 5.85 million BTUs of heat energy. Therefore, exploiting methane clathrate beds could be made economically viable if existing equipment is used and natural gas is priced between \$4 and \$6 per thousand cubic feet (Ruppel, 2007). Also of interest, the combustion reaction for methane is much cleaner than most other hydrocarbon fuel sources. Combustion of methane with air produces lesser amounts of CO_2 , CO , SO_2 , and NO_x s compared to other combustion reactions. From all this information, it is clear that methane hydrates are becoming a more and more attractive alternative to oil.

Extraction Technology

Methane clathrate beds are very extensive, and although there may be large volumes of proven trapped gas reserves, a major problem is that the hydrate density of any particular location is usually not high (Ruppel, 2007). While the direct gathering of solid methane hydrates would be impractical due to low unit per volume concentrations, several ideas have been postulated for the extraction of methane from hydrate beds. All methods rely on creating a slow controlled dissociation process that will lead freed gas to a drilled bore hole. First of all, any possible extraction site will have to be extensively well studied, and extraction techniques would have to be proven safe, efficient, cost effective, and environmentally friendly. Once those criteria are met, there are three main methods by which hydrate gases may be collected.

A: Gases may be collected by thermal stimulation. An influx of hot water or steam would partially melt the hydrate beds in ocean sediments or in permafrost regions. The hot fluids would be pumped down into the

hydrate layers, and the liberated gases would flow to the bore hole where they ascend through the pipe up to the surface. An advantage of this method is that it is simple and would be conceivably easy to do. However, the major disadvantage is that heating the fluids to pump underground would be cost prohibitive and might not reach deeper hydrate sediments (Ruppel, 2007).

B. Another option is depressurization of hydrates in sediment beds. This would be done by drilling deep into clathrate beds where methane can exist in the free gas stage before being converted to hydrates. The idea here is that a change in the local pressure gradient within the sediment beds will cause the gases to flow freely to a well head. This strategy could be the easiest way to collect hydrate gases as the process would be self-driving, but it has the disadvantage of being more unpredictable than any other methods. Also, the dissociation of clathrate crystals is very endothermic having an enthalpy of dissociation value of +55KJ/mol at 273K. A depressurization so rapid could cool sediments and machinery to the point they might freeze, clog, and malfunction (Ruppel, 2007).

C. An alternative strategy purposes to collect hydrate gas by the injection of an inhibiting fluid into sediment beds via a well head. The inhibiting fluid may consist of solutions of methanol, ethanol, glycol, or brines, and these fluids work to dissociate gas hydrates by altering the chemical composition of the local pore water to no longer favor hydrate stability. These chemicals would lower the freezing point of water in the vicinity, free trapped gases, and the gases would again be collected by the same well head. An immediate disadvantage of this process is that it might be environmentally dangerous if hydrate solvents other than salt brines are used. This concept has the advantages that dissociation rates theoretically could be controlled by adjusting amounts of inhibitor fluids. The inhibitor fluids would also prevent hydrates from clogging pipelines and well heads during collection (Ruppel, 2007).

An interesting application of the inhibitor injection process is that carbon dioxide could possibly be used as a dissociant. Carbon Dioxide could be used in harvesting of natural gas as well as sequestering carbon dioxide out of atmospheric circulation because CO₂ can replace Methane in clathrates (Ruppel, 2007). While the technology used in extracting methane from hydrate beds is still experimental, it does exist and has been proven. Ruppel states that “the first verifiable production

of natural gas from methane hydrate probably occurred during depressurization and thermal injection tests conducted at the Mallik permafrost well in 2002.” He goes on to say that the amount of gas produced at the Mallik well in the Northwest Territories of Canada wasn’t the important factor, but that the experimental extraction proved that existing drilling technologies can be used to collect natural gas from hydrate sources. The experiment provided data about techniques, production rates, well control, and the usefulness of computer models in predicting rates of gas extraction.

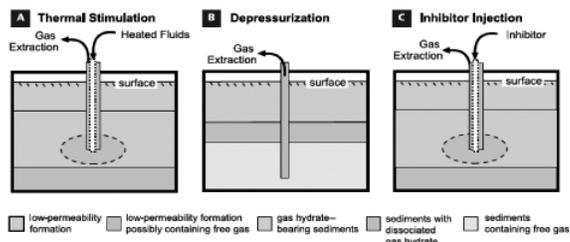


Figure 5 (Ruppel, 2007)

Problems

There are, however, some challenges associated with producing natural gas of any origin. The biggest issue is transportation. Natural gas is usually transported by pipeline or tanker truck as a liquid. Liquefied Natural Gas (LNG) has the danger of exploding due to an ignition source or simply a pressure rupture. LNG has the added disadvantage that it has to be liquefied in order to economically transport quantities of it, and that process is time-consuming and costly. Today, most natural gas is utilized to power existing infrastructures on site, and it is not shipped long distances to consumers. If methane hydrates are collected and used as a general energy source, improved methods of storage and transportation of the LNG will need to be developed.

Furthermore, methane represents an added danger in that it is 20 times more powerful as a greenhouse gas than carbon dioxide is. Great care would have to be taken that no substantial release of methane into the atmosphere could occur. Also, considerable methane release in a marine environment into the water column would alter pH, CO₂ solubility, carbonate formation, and dissolved O₂ levels.

Another potential danger exists in what has been popularized as the “Clathrate Gun Hypothesis” whereby a catastrophic methane release into our atmosphere is thought to have caused a climate change and mass extinctions. Schiermeier explains that “a catastrophic release of trillions of tonnes of methane is thought to have triggered a temperature jump some 55 million years ago in an already warm climate at the Palaeocene/Eocene boundary” (Schiermeier, 2006). However, new data regarding the deuterium isotope content of methane trapped in bubbles of a Greenland ice core seems to show that no large spike in atmospheric methane content occurred at that time. Therefore, the so called “Clathrate Gun Hypothesis” is now considered unlikely (Schiermeier, 2006).

Interestingly enough, it has been shown that large methane releases from marine sediments do occur on smaller scales and that these small methane bubble releases can pose a threat to ships and airplanes in areas of high methane concentration. In fact, the seabed near the southern tip of Florida has been shown to have had large clathrate beds that have burst open and suddenly released large amounts of methane. Correspondingly, aircraft engines have been shown to suddenly stall and fail in atmospheric concentrations of methane as low as 1%. Therefore, these facts in tandem have led some people to suspect that the cause of the infamous Bermuda Triangle ship and airplane disappearances was at least partially due to methane eruptions from the seabed (Salleh, 2003). It is clear that methane hydrates need to be better understood and studied before any major large scale extraction of their gases is attempted.

Conclusion

Methane clathrates are an important mineral that can be found in marine sediment beds on continental shelves all around the world. The unique chemistry of gas clathrates makes it possible for even the most unreactive gases like dinitrogen and noble gases to participate in altering the chemical properties of substances in a perceptible way. Being partially held together by pressure and Van der Waals forces, hydrate beds tend to be very unstable, and they can suddenly release large quantities of methane gas into the ocean and atmosphere. Nonetheless, hydrate beds represent a major carbon reservoir on our planet even though large amounts of methane have the potential to escape their clathrate cage rather rapidly. Methane escaping from the sea bed has been blamed for everything from global warming to mass extinctions, and the Bermuda Triangle. If one thing is known about gas hydrate beds with certainty, it is that there are a lot of them on our planet. In many, tapping methane hydrate beds as an energy source would be a positive occurrence for our government, economy, and industry. However, the potential for this large untapped energy source is not without its significant draw-backs and risks. There is a great deal of concern over whether utilizing methane hydrates as a natural resource would be safe or cost effective. Clearly, more scientific research and engineering needs to go into looking at the problems associated with methane hydrates before any large-scale extraction is attempted.

WORKS CONSULTED

- Dillon, William. Gas (Methane) Hydrates -- A New Frontier. United States Geological Survey. September 1992. 3/8/08. <http://marine.usgs.gov/fact-sheets/gas-hydrates/title.html>
- Garg, Sabodh K. Pritchett, John W. Katoh, Arata. Baba, Kei. Fujii, Tetsuya. A Mathematical model for the Formation and Dissociation of Methane Hydrates in the Marine Environment. Journal of Geophysical Research, VOL. 113. 2008.
- Hornberger, George M., Jeffrey Raffensperger, Patricia L. Wiberg, and Keith N. Eshleman. Elements of Physical Hydrology. Baltimore: The Johns Hopkins University press, 1998.
- Mielke, James E. Methane Hydrates: Energy Prospect or Natural Hazard? CRS Report for Congress. 2000. 3/8/08. <http://www.ncseonline.org/nle/crsreports/energy/eng-46.cfm>
- Pfeffer, John T. "Biological Conversion of Biomass to Methane." U.S. Department of Energy. 1978.
- Rayner-Canham, Geoff. Overton, Tina. Descriptive Inorganic Chemistry. 4th Ed. New York: W.H. Freeman and Company. 2006.
- Ruppel, Carolyn. Tapping Methane Hydrates for Unconventional Natural Gas. Elements; June 2007. v. 3; no. 3; 3/9/08. p. 193-199.
- Salleh, Anna. "Giant Bubbles Could Sink Ships." ABC Science Online. Oct. 24, 2003. 4/18/08. <http://dsc.discovery.com/news/afp/20031020/methane.html>
- Schiermeier, Quirin. Methane burps disproved? Nature News. BioEd Online. MacMillan publishers Ltd. 2006. <http://www.bioedonline.org/news/news.cfm?art=2334>
- Tomaru, Hitoshi. Lu, Zunli. Fehn, Udo. Muramatsu, Yasuki. Matsumoto, Ryo. "Age Variation of Pore Water Iodine in the Eastern Nankai Trough, Japan: Evidence for Different Methane Sources in a Large Gas Hydrate Field." Geology, November 2007; v.35; no. 11; p. 1015-1018. 3/8/08.
- United States. Science Support Program (U.S.S.S.P.). What is Scientific Ocean Drilling? Washington: JOI, 2005. http://www.usssp-iodp.org/Images/flaming_hydrate.jpg.
- Yakushev V.S., Istomin V.A.. What Are Gas Hydrates? 2003. 4/19/08. http://www.geol.msu.ru/deps/cryology/index_h_en.htm